AN OVERVIEW OF UNOCAL'S LOW EMISSIONS GASOLINE RESEARCH PROGRAM

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SINCE THE MID-1980s, oil companies, government agencies and automobile manufacturers have extolled the emissions improvements possible by changing the composition of gasolines used in spark ignition engines. The promise has been that, by changing the composition and physical properties of fuels, vehicle emission systems will work more cooperatively with the fuel to limit the output and reactivity of pollutants.

Some regulations which specify fuel formulations as a method for emissions reduction from automobile exhausts are currently in effect. For example, several western states that are unable to meet regulated wintertime carbon monoxide (CO) levels for ambient air quality standards, as prescribed in the Clean Air Act, already impose mandatory oxygen content of gasoline. Other regulations being considered include the reduction of Reid vapor pressure to limit the evaporative emissions of hydrocarbons from vehicles.

It was the purpose of the work described here to evaluate a fuller set of fuel properties than has previously been done to gain a more complete understanding of the interactions between fuels and emissions systems. Our program was unique in that there was a greater focus on the fuel matrix design than in any other previously published work. We pursued our emissions testing using a linear screening design for the fuels in which ten properties were varied independently within the bounds placed by four multivariable contraints (see Table 1). No up-front assumptions were made as to which gasoline properties were important.

The fuels we prepared for this program had chemical compositions typical of gasolines sold in commerce. These gasolines were made from eleven gasoline blending stocks which are widely used in refineries. All blends included a highly effective gasoline detergent to minimize deposit related deterioration of the fuel, engine and emission system. All car/fuel combinations were tested at least twice in random order. Other constraints which have been included in these fuels are limitations on the octane sensitivity (RON-MON) and distillation properties of the blends to make the products more typical of commercial gasolines. These constraints limited the possibility of designing a gasoline that improved emissions while limiting the performance of the vehicle in other areas. Finally, a limit was placed on the amount of aromatics plus MTBE present in any blend so that octane was limited to normal levels.

The fuels were each run at least twice in random order, including no back to back duplication, to limit systematic errors and effects from uncontrolled variables. A control fuel was run frequently to evaluate possible time sequence error. This showed that no significant changes were seen in any individual vehicle emissions over the time span of our experiments.

Results from two separate emission test programs using the fifteen fuel test matrix have shown that changes in gasoline distillation characteristics, olefin content and Reid vapor pressure

(RVP) can produce major changes in total tailpipe exhaust emissions. All other variables examined, including oxygen content and aromatic content of the fuels, did not directly or greatly affect the tailpipe emissions of carbon monoxide, nitrogen oxides, or hydrocarbons. From these results a generalized mathematical model was produced which predicts tailpipe emission changes from key fuel properties. The model was verified in a separate, 13 vehicle study.

The single vehicle test program was performed with a 1988 Oldsmobile Regency 98 equipped with a current technology closed-loop three-way catalyst and adaptive learning emission system. Sixty three FTP tests were performed in this vehicle during this stage of our experimentation. The car was selected because it represented a high sales volume product that was close to current state of the art in emission technology.

This vehicle is representative of those that use the technology in which it would be expected to be most difficult to effect gross emissions by changing the fuel. This is because the emissions from this vehicle are already very low and there are limited effects one might expect from fuel compositional changes. Further, the adaptive learning feature of this technology tends to reduce the effect of changing fuel composition. Finally, tests were run in this car because it was felt that it contained the major types of vehicle emission technology that will be in the marketplace in the mid-1990s and beyond. Major changes in gasoline composition would take until the mid- to late-1990s, at the minimum, to implement.

All emissions testing was performed in the Unocal emissions testing facility in Brea, California. The fifteen fuel test matrix that was used was uniquely designed to screen 10 properties independently through a linear screening, statistical designed experiment. Emissions of carbon monoxide (CO), hydrocarbons (HC) and oxides of nitrogen (NOx) were determined with the 1975 Federal Test Procedure (FTP). Changes by a factor of 1.5 to 3.0 in these emissions were observed across the range of test gasolines used. The main variables that we found that affect the FTP tailpipe emissions are distillation characteristics, olefin content, and RVP. The results of these experiments strongly suggest that through simple changes in the formulations of gasolines, fuel and vehicle systems can work more effectively together, producing less total emissions.

Figures 1, 2, and 3 show the hydrocarbon, carbon monoxide, and nitrogen oxides emissions, respectively, observed for the Oldsmobile Regency 88 over the range of the 15 experimental design fuels. The average of two or more independant measurements on each fuel are plotted with 95% confidence intervals. The confidence intervals were calculated using a pooled standard deviation over all the fuels so all confidence intervals are identical. Also plotted, as a horizontal reference line on each Figure, are the average emissions observed for the Auto/Oil RF-A, industry average gasoline (1), flanked with 95% confidence interval reference lines . This fuel is identical to the reference gasoline described in the 1991 Clean Air Act.

It can readily be seen from an examination of the confidence levels on these three Figures that the range of observed emissions, relative to the repeatability of the experimental data, is high. In addition, while the observed order of fuels, from lowest to highest, is similar, but not identical, for hydrocarbon (HC) and carbon monoxide (CO) emissions, it is quite different for nitrogen oxides (NOx) emissions.

This way of presenting the experimental data leads to the observation that quite different fuel properties are controlling NOx emissions compared to the HC and CO emissions, but that the properties controlling HC and CO emissions are probably similar.

The set of linear models that fits this single car data quite well are as follows:

$$HC\ (gm/mile) = 0.00245(olefins\ vol\%) + 0.00109(T_{50}) - 0.00104(RON)$$
$$CO\ (gm/mile) = 0.00937(T_{50}) + 0.00133(T_{90}) - 0.00828(saturates\ vol\%)$$
$$NO_x\ (gm/mile) = 0.00503(olefins\ vol\%) - 0.0006(saturates\ vol\%) + 0.00087(T_{10}) + 0.0159(RVP)$$

Fitting the experimental data is only one measure of the value of these equations. A second measure is their ability to make predictions about fuels not in the experimental matrix. Table 2 contains the observed properties of four gasolines that were used as check points to test the predictive equations. At least two FTP runs were made using each of these four fuels. A comparison between average measured and predicted emissions for each fuel is shown in Table 3. This shows that, at least for these four fuels, the predicted emissions are always within two standard deviations of the mean measured emissions.

The startling range of emissions observed over our set of test fuels, coupled with the success of simple linear models in predieting emissions of gasolines outside the test fuel set used to generate the models, lead to the conclusion that the properties of gasolines can have a dramatic effect on tailpipe emissions. This prompted the aquisition of a ten car fleet to test our single-car conclusions for generality.

The confirmatory ten car fleet test was run at Southwest Research Institute in San Antonio, Texas. In this test fifteen fuels, with similar fuel characteristics to those used in the single car experiment, were evaluated using the FTP. The ten cars tested were selected from the list of post-1980 model vehicles used in the Auto/Oil test fleet (1). Details of the fleet are shown in Table 4. The results supported the conclusions from the single car study. Olefins, RVP and distillation were major influences of vehicle emissions over the entire ten car fleet.

Fifteen new test gasolines were blended in accordance with those used in our previous single car test. Again, they were designed to vary each of the ten properties, shown in Table 1, independently. New blending stocks for these fuels were obtained from the Unocal Los Angeles refinery. Physical characteristics had changed slightly over our initial blending streams, so the final blends produced varied slightly in physical properties from our fifteen initial blends. The experimental protocol was identical to that used in the testing performed with the single car described above.

Preliminary analysis of the FTP data showed that the older technology cars responded to fuel changes differently to the newer cars. Consequently, for further analysis the fleet was split into two catagories. The Suburban, Tempo, Caprice, and Accord were grouped together as older technology cars while the remaining six cars were grouped as newer technology vehicles.

The data confirmed some of the observations made concerning the emissions of the single car in our earlier program. For all ten cars we have seen very big changes in bulk emissions as we

have varied fuel properties within our experimental design set of gasolines. We observe spreads between lowest and highest emissions by factors of 1.5 to 2 on a fleet averaged basis.

Initial regression analysis of the emissions data outlined above using the cars as groups was not very satisfactory. For example, regression models tended to give poor predictability. To get around this we reverted to the type of analysis that was completed for the single car study. We built individual, empirical regression models for each car. The results of these regression analyses are shown in Tables 5, 6, and 7. These Tables show which variables have a significant effect on HC, CO, or NOx emissions respectively, by car. In the Tables, a + indicates a property that has the effect of raising the tailpipe emission if the value of that property is increased. Similarly, a - indicates that if the property value is increased, the associated emission decreases.

It is readily apparent from these Tables that the property that has the most universal effect is on HC and CO emissions is the distillation T_{50} point. For NOX emissions there were three properties with almost universal effect. These were olefin content, distillation T_{10} point, and Reid vapor pressure (RVP).

There are many ways in which individual car effects can be combined to yield a predictive equation for the fleet. We chose to combine individual regression equations by taking simple averages of all the individual car equations. This gave the following set of three equations:

HC = -0.000474(aromatics vol%) + 0.00248(olefins vol%)
- 0.00212(research octane number) + 0.00207(T_{50} distillation point)

CO = -0.00682(saturates vol%) + 0.0128(T_{50} distillation point) + 0.00123(T_{90} distillation point)

NOx = 0.005595(olefin vol%) - 0.000282(saturates vol%)
+ 0.002715(T_{10} distillation point) + 0.02765(Reid vapor pressure)

In order for this predictive model to be useful to a refiner the model needs to be capable of predicting formulations that meet emissions reduction targets that can be blended in the refinery. We set up to run our Los Angeles refinery using the predictive model as part of the refinery linear program (LP). The goal was to produce a fuel that had a emissions of 15% below the emissions of the CAA reference gasoline. A premium unleaded gasoline was formulated for testing that was part of the overall refinery balance. Properties of the experimental and reference fuels are shown in Table 9.

The testing was performed at Southwest Research Institute vehicle emissions test facility in San Antonio, Texas and NIPER's emission test facility in Bartlesville, Texas. Exhaust emissions were evaluated through the EPA's 1975 Federal Test Procedure (FTP).

Thirteen vehicles were selected to represent the major vehicle emission technology classes since 1970 and to mimic the present day California fleet. These vehicles are listed in Table 8. The experimental protocol was identical to that used in the testing performed with the single car described above.

The results of this strategy are shown in Figure 4. In this Figure the average emissions reductions of all 13 cars, along with pooled 85% confidence levels, are plotted for the experimental gasoline. These reductions are shown as a percentage of the reference gasoline emissions levels. The 85% confidence levels for the reference fuel are shown as a variable-width band across the center of the chart, centered about zero. The 85% confidence level was chosen for this comparison because, at the time, it was the value that the California Air Resources Board was contemplating using for this type of comparison.

The experimental emissions reductions for the whole 13 car fleet are plotted as three vertical bars at the left side of the chart. It can be seen that we achieved the substantial emissions reduction that we were aiming for. Not only did we greatly reduce both HC and CO emissions but we *SIMULTANEOUSLY* reduced NOx emissions.

Although the HC and CO emissions reductions met our expectations, the overall NOX emissions reduction did not. Considering that the predictive equations we used were based on data collected with post-1980 cars, we decided to split this experimental data and recalculate NOx emissions reductions for two groups of cars. These reductions are plotted as vertical bars on the right side of the chart in Figure 4. The 13 car fleet was split into its pre-1980 and post-1980 components.

The result of this exercise shows that we did indeed achieve the NOx emissions reductions that we had expected, but only in the post-1980 fleet. That is, in the cars with the types of technology that we had done all our previous experimental work with. In the older cars the test gasoline exhibited NOx emissions that were not statistically different from the NOx emissions of the reference fuel. We believe that this difference in NOx emissions between the older and newer car fleets may be caused by the presence of oxygenate in the test gasoline. This would be in agreement with published literature concerning the effect of oxygenates on the emissions from pre-1980 cars (2).

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Table 1

Fuel Variables And Their Ranges

Variable or Constraint	Min.	Max.
aromatics (vol%)	10	45
olefins (vol%)	0	15
paraffins (vol%)	40	90
MTBE (vol%)	0	15
Research Octane # (RON)	90	95
Motor Octane # (MON)	84	87
Distillation 10% Point (°F) T10	130	160
Distillation 50% Point (°F) T50	170	240
Distillation 90% Point (°F) T90	290	350
Reid Vapor Pressure (psi) RVP	8	10
RON-MON	5	8
Aromatics + MTBE	0	50
T50 - T10	50	
T90 - T50		150

Table 2

Check Fuel Properties

Property	#1	#2	#3	#4
aromatics (vol%)	40.9	20.7	58.3	30.0
olefins (vol%)	11.1	10.8	0.4	9.2
paraffins (vol%)	48.0	61.4	30.4	60.8
MTBE (vol%)	0.0	7.1	10.9	0.0
RON	96.4	92.8	107.0	92.1
MON	85.2	84.0	95.7	82.4
T10	120	125	160	112
T50	214	198	218	200
T90	339	348	229	315
RVP	8.2	8.0	5.4	8.7

Table 3

Check Fuel Emissions

Emission	Fuel #	Measured g/mile	Calculated g/mile	Difference g/mile	Standard Deviation
Carbon Monoxide	1	2.127	2.059	0.067	0.205
	2	1.584	1.810	0.226	
	3	1.901	2.096	0.195	
	4	2.319	2.009	0.310	
Nitrogen Oxides	1	0.266	0.261	0.005	0.016
	2	0.263	0.256	0.007	
	3	0.200	0.207	0.007	
	4	0.286	0.260	0.026	
Hydro-carbons	1	0.178	0.161	0.017	0.014
	2	0.139	0.146	0.007	
	3	0.142	0.126	0.014	
	4	0.189	0.165	0.024	

Table 4

Ten Vehicle Fleet Details

OEM	Model	Engine Size (ℓ)	Fuel System[1]	EGR[2]	Catalyst System	Year
GM	Cutlass	2.3	PFI	no	3-way	1989
GM	98 Regency	3.8	PFI	yes	3-way	1988
Ford	Tempo	2.3	TBI	yes	3-way	1985
Ford	Lincoln	5.0	PFI	yes	3-way, dual bed, close coupled	1990
GM	Caprise	2.0	Carb	yes	3-way, dual bed	1984
Honda	Accord	2.0	Carb	yes	3-way	1988
Ford	Taurus	3.0	PFI	no	3-way, close coupled	1989
Dodge	Shadow	2.5	TBI	yes	3-way, close coupled	1990
GM	Suburban	2.5	Carb	yes	oxidation	1985
Toyota	Camry	2.0	PFI	yes	3-way, close coupled	1990

1) PFI = Port Fuel Injected, TBI = Throttle Body Injected, Carb = carburetted

2) EGR = Exhaust Gas Recirculation

Table 5

Individual vehicle effects of fuel properties in the 10 car fleet on **Hydrocarbon** emissions

Car	arom vol%	olef vol%	RON	T50
GM Cutlass		+	-	+
GM 98 Regency			-	+
Ford Tempo			-	+
Ford Lincoln	-			+
GM Caprice	-			+
Honda Accord	-			+
Ford Taurus		+	-	+
Dodge Shadow	-			+
GM Suburban	-			+
Toyota Camry		+	-	+

Table 6

Individual vehicle effects of fuel properties in the 10 car fleet on **Carbon Monoxide** emissions

Car	arom vol%	para vol%	T50	T90
GM Cutlass		-	+	
GM 98 Regency		-	+	
Ford Tempo		-	+	
Ford Lincoln			+	
GM Caprice	-		+	
Honda Accord			+	
Ford Taurus			+	
Dodge Shadow		-	+	+
GM Suburban		+	+	-
Toyota Camry		-	+	

Table 7

Individual vehicle effects of fuel properties in the 10 car fleet on **Nitrogen Oxide** emissions

Car	olef vol%	paraf vol%	T10	RVP
GM Cutlass	+	-	+	+
GM 98 Regency	+		+	+
Ford Tempo	+		+	+
Ford Lincoln	+		+	+
GM Caprice	+		+	+
Honda Accord	+	-	+	+
Ford Taurus	+		+	+
Dodge Shadow	+		+	+
GM Suburban	+		+	+
Toyota Camry	+		+	

Table 9

Reference and Reformulated Gasoline Properties

Property	Reformulated Premium Gasoline	CAA Reference Gasoline
aromatics (vol%)	44.1	32.0
olefins (vol%)	3.3	9.2
paraffins (vol%)	45.4	58.8
mtbe (vol%)	7.2	0.0
RON	97.5	92.0
T10 (°F)	136	128
T50 (°F)	208	218
RVP (psi)	8.0	8.7

Table 8

13 Car Fleet Details For Reformulated Commercial Gasoline Test Program

OEM	Model	Engine Size (l)	Fuel System[1]	EGR	Catalyst System	Year
GM	98 Regency	3.8	PFI	yes	3-way	1988
Ford	Tempo	2.3	TBI	yes	3-way	1985
Ford	Lincoln	5.0	PFI	yes	3-way, dual bed, close coupled	1990
Honda	Accord	2.0	Carb	yes	3-way, dual bed	1988
Toyota	Camry	2.0	PFI	yes	3-way, close coupled	1990
Dodge	Shadow	2.5	TBI	yes	3-way, close coupled	1990
Chrysler	Diplomat	5.2	Carb	yes	oxidation	1979
GM	Monte Carlo	5.0	Carb	yes	oxidation	1978
GM	Caprice	5.7	Carb	yes	oxidation	1979
GM	Delta 88	7.4	Carb	yes	non-catalyst	1974
Ford	LTD	6.6	Carb	yes	non-catalyst	1974
Chrysler	Dart	3.7	Carb	yes	non-catalyst	1973
Ford	Cougar	5.8	Carb	yes	oxidation	1975

1) PFI = Port Fuel Injected, TBI = Throttle Body Injected, Carb = carburetted.

Figure 1
Hydrocarbon Emissions of Experimental Fuels
in Oldsmobile 98 Regency

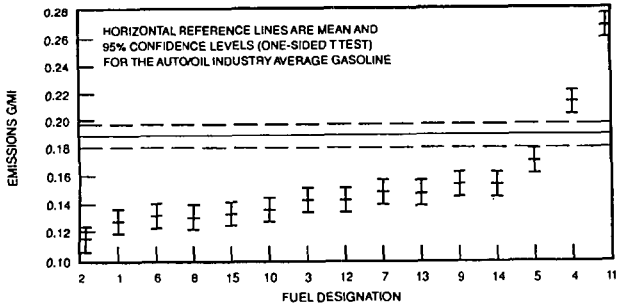

Figure 2
Carbon Monoxide Emissions of Experimental Fuels
in Oldsmobile 98 Regency

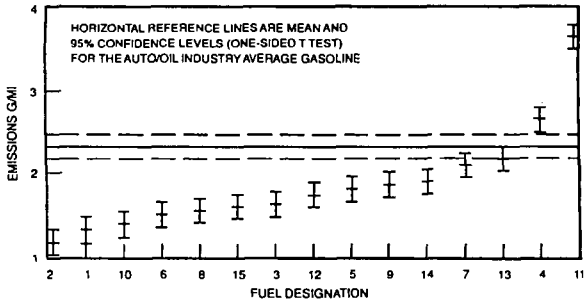

Figure 3
Nitrogen Oxide Emissions of Experimental Fuels
in Oldsmobile 98 Regency

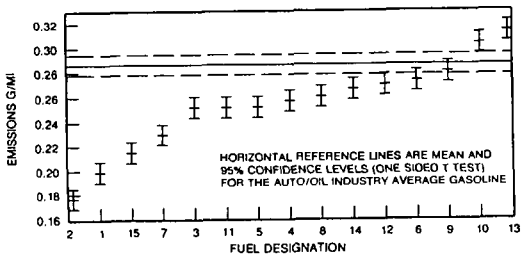

Figure 4
Comparison of Emissions of Predicted Low Emission Gasoline
With the CAA Reference Gasoline